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14. ABSTRACT During the course of this ARO project we proposed [J. Chem. Phys. 135, 024201 (2011)] that using stimulated Raman adiabatic passage (SARP) with partially overlapping pump and Stokes laser pulses it is possible to transfer the complete ground state population of an isolated diatomic molecule to an excited rovibrational eigenstate. Based on this idea we carried out experiments using a sequence of overlapping pump (532 nm) and Stokes (683 nm) single-mode laser pulses of unequal fluence to prepare isolated H2 molecules in a molecular beam. In a first series of experiments we were able to transfer more than half the population of H2 ($v=0, J=0$) level to an excited					
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Report Title

Preparation of Quantum States of H₂ using Stark-induced Adiabatic Raman Passage (SARP)

ABSTRACT

During the course of this ARO project we proposed [J. Chem. Phys. 135, 024201 (2011)] that using stimulated Raman adiabatic passage (SARP) with partially overlapping pump and Stokes laser pulses it is possible to transfer the complete ground state population of an isolated diatomic molecule to an excited rovibrational eigenstate. Based on this idea we carried out experiments using a sequence of overlapping pump (532 nm) and Stokes (683 nm) single-mode laser pulses of unequal fluence to prepare isolated H₂ molecules in a molecular beam. In a first series of experiments we were able to transfer more than half the population of H₂ ($v=0$, $J=0$) level to an excited rovibrational level [J. Chem. Phys. 138, 051101-1-4 (2013)]. Since then, we have achieved almost complete transfer (97 ± 7%) of population from the H₂ ($v=0$, $J=0$) ground rovibrational level to the H₂ ($v=1$, $J=0$) excited rovibrational level [W. Dong, N. Mukherjee and R. N. Zare, J. Chem. Phys. 139, 074204 (2013)]. SARP opens new avenues to explore reaction dynamics using single or coherent superposition of quantum states.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/25/2011	2.00 Nandini Mukherjee, Richard N. Zare. Stark-induced adiabatic Raman passage for preparing polarized molecules, The Journal of Chemical Physics, (07 2011): 24201. doi:
08/28/2012	3.00 Nandini Mukherjee, Richard N. Zare. Can stimulated Raman pumping cause large population transfers in isolated molecules?, The Journal of Chemical Physics, (11 2011): 0. doi: 10.1063/1.3657832
09/14/2010	1.00 Nandini Mukherjee and Richard N. Zare. Polarization of molecular targets using infrared stimulated Raman adiabatic passage, Journal of Chemical Physics, (09 2010): . doi:
11/26/2013	4.00 Nandini Mukherjee, Wenrui Dong, John A. Harrison, Richard N. Zare. Transfer of more than half the population to a selected rovibrational state of H ₂ by Stark-induced adiabatic Raman passage, THE JOURNAL OF CHEMICAL PHYSICS, (02 2013): 51101. doi:
11/26/2013	5.00 Wenrui Dong, Nandini Mukherjee, Richard N. Zare. Optical preparation of H ₂ rovibrational levels with almost complete population transfer, THE JOURNAL OF CHEMICAL PHYSICS, (08 2013): 74204. doi:
TOTAL:	5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Richard N. Zare	0.00	Yes
FTE Equivalent:	0.00	
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Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Nandini Mukherjee	1.00
FTE Equivalent:	1.00
Total Number:	1

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Inventions (DD882)

Scientific Progress

Technology Transfer

Preparation of Quantum States of H₂ using Stark-induced Adiabatic Raman Passage (SARP)

It is well known that the spatial orientation of two approaching reagents dynamically modifies their interaction potential, thus changing the barrier to reaction. In a benchmark chemical reaction like H₂ + H comparison between experiment and theory continues to be hampered by statistical averaging over the initial states of the molecular hydrogen reagent. To our knowledge a stereodynamical reaction has never been possible with a precision of a single *M*-state of H₂. To understand and control reaction dynamics at the most fundamental level we focus on preparing the H₂ molecular target in specific quantum states. Because of the large energy gap (~ 11 eV) between the ground and accessible excited electronic states, so far it has been a frustrating challenge to populate selected rovibrational *M*-states within the electronic ground state of a H₂ molecule. To accomplish this goal, recently we proposed a new coherent laser excitation technique [Mukherjee & Zare, *J. Chem. Phys.* **135**, 024201], called the Stark induced adiabatic Raman passage (SARP) which promises, for the first time, to transfer the entire ($\nu = 0, J = 0$) ground-state population of H₂, HD, or D₂ to a single *M* quantum state of an excited rovibrational energy eigenstate ($\nu > 0, J$). This unprecedented control of reagent state will allow us to study stereodynamic processes that previously have been hidden by the average over all *M* states in unpolarized reagent collisions. The basic idea of SARP is shown in Fig. 1.

Stark-Induced Adiabatic Raman Passage (SARP)

A strong pump followed by weaker Stokes pulse (or, vice versa)
transfers **all** population to desired quantum state

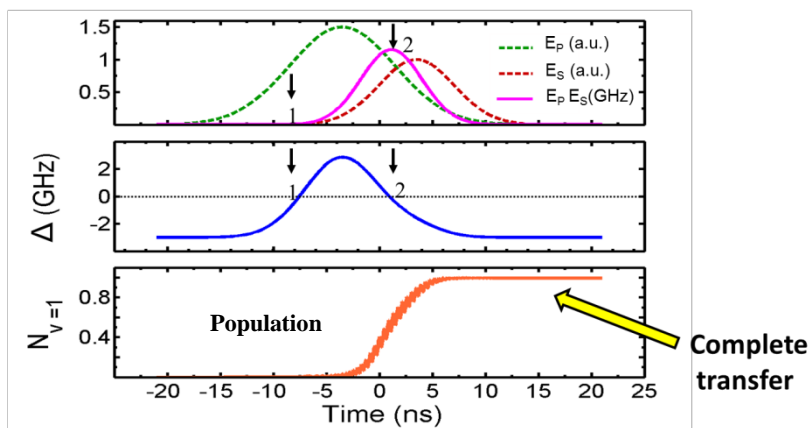


Figure 1

SARP-Idea: Mukherjee & Zare, *J. Chem. Phys.* **135**, 024201 (2011)

SARP uses a sequence of partially overlapping off-resonant nanosecond pump and Stokes pulses of unequal intensities (green and red dashed in upper panel of Fig. 1). The pulse with the higher intensity (pump or Stokes) generates the necessary sweep (Δ in middle panel) of the Raman resonance frequency by inducing second-order (dynamic) Stark shifts of the rovibrational levels. During the pulsed excitation the Raman transition frequency is swept through resonance twice as shown by the arrows in the middle panel of Fig. 1. The delay between the pulses is adjusted so that only one of these crossings (second one) is avoided with significant Raman coupling (purple in panel 1, $\propto E_P E_S$ overlap of pump and Stokes pulses). As the Raman resonance is crossed with sufficiently strong Raman coupling, a unidirectional flow of population from the initial to the final target state takes place during the overlap of the pump and Stokes pulses as shown in the lower panel of Fig. 1. Based on this idea we carried out experiments by combining a single-mode pump pulse (532 nm, 6 ns) with a single-mode dye laser pulse (683 nm, 4.6 ns) with a relative delay of 4-6 ns as shown in Fig. 2.

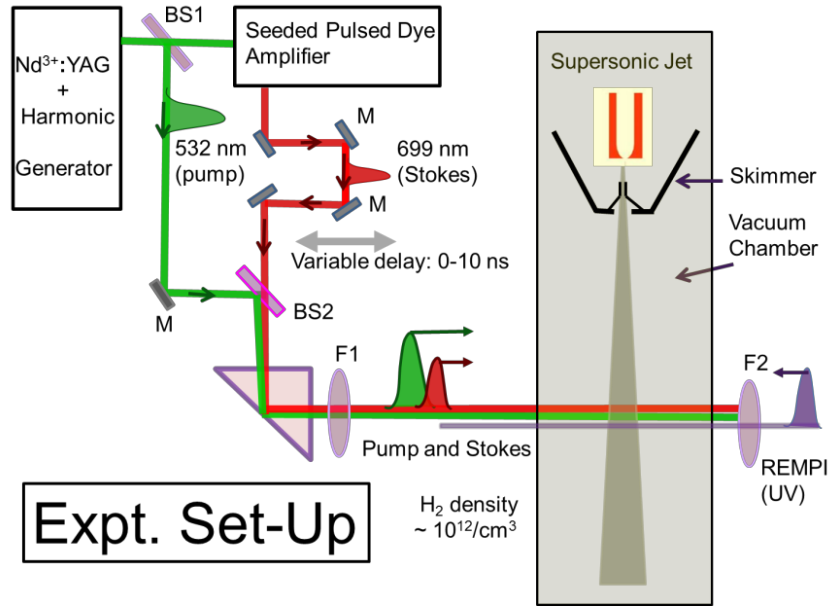


Figure 2. Excitation of H_2 molecular beam using delayed sequence of pump and Stokes pulses.

Pump pulse: 6 ns, 532 nm, $10 J/mm^2$; Stokes pulse: 4.6 ns, 683 nm, $1 J/mm^2$

The delayed sequence of pump and Stokes pulses transversely intersects a supersonic beam of H_2 molecules within a vacuum chamber. Following SARP excitation, H_2 molecules are probed state selectively using (2+1) resonance enhanced multiphoton ionization (REMPI) via the bound-bound $E, F^1\Sigma_g^+(v'=0, J'=J) - X^1\Sigma_g^+(v=0, 1, J)$ transition. . In a first series of experiments we were able to transfer more than half the population of H_2 ($v=0, J=0$) level to an excited rovibrational level [J. Chem. Phys. **138**, 051101 (2013)]. Since then, we improved the experimental conditions achieving nearly complete population transfer from H_2 ($v=0, J=0$) \rightarrow H_2 ($v=1, J=0$) as exhibited in Fig. 3 [J. Chem. Phys. **139**, 074204 (2013)]. The top panel in Fig. 3 shows the (2+1) REMPI signal from the vibrationally excited ($v=1$) level. The background-free ($v=1$) REMPI signal does not allow us to calibrate the fractional population transfer from ($v=0$) \rightarrow ($v=1$). The population transfer is calibrated from the depletion of ($v=0$) REMPI signal ((b) and (c) of Fig.3), which yields nearly complete transfer from ($v=0$) \rightarrow ($v=1$) when the background is properly subtracted (lowest panel).

SARP pumping of H_2 ($v=0, J=0, M=0$) \longrightarrow H_2 ($v=1, J=0, M=0$)

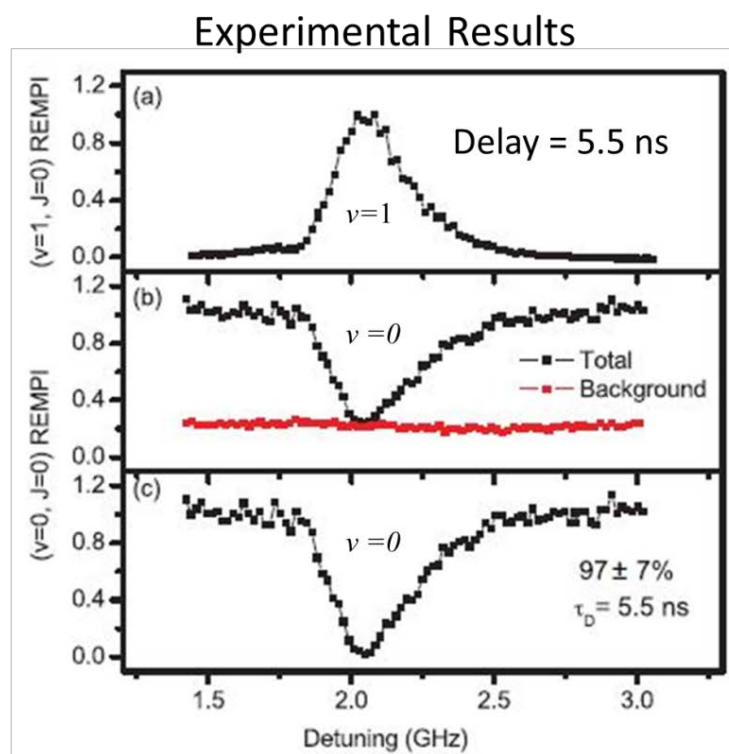


Figure 3. H_2 ($v=0, J=0$) \rightarrow (H_2) ($v=1, J=0$) Complete Population Transfer

Dong, Mukherjee & Zare, J. Chem. Phys. **139**, 074204 (2013)

Figure 4 shows SARP population transfer at various delays, confirming that maximum population transfer over the widest range of frequency is achieved not at zero-delay but at a relatively large delay of 5-6 ns between the pump (6 ns) and Stokes pulses (4.6 ns).

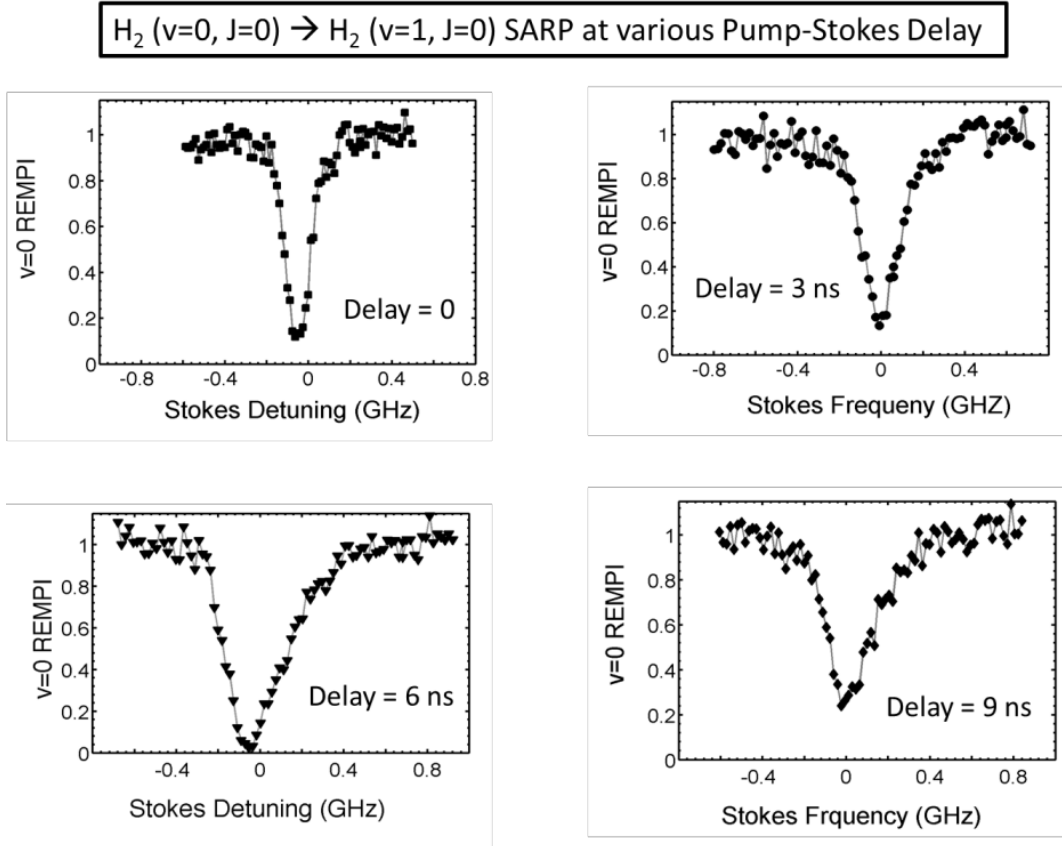


Figure 4. $H_2(v=0, J=0) \rightarrow H_2(v=1, J=0)$ Population Transfer maximizes at large delay

Dong, Mukherjee & Zare, *J. Chem. Phys.* **139**, 074204 (2013)

Preparation of Vibrationally Excited M-state Superposition of H_2

By combining different polarization states of the pump and Stokes laser pulses SARP prepares superposition of M-eigenstates with a rovibrational (v, J) energy eigenstate as follows:

$$|\psi(t)\rangle = \sum_M C_M |v > 0, J, M\rangle \quad (1)$$

As opposed to wave-packets, the above superposition is a stationary state evolving with a single frequency $\frac{E_{vJ}}{\hbar}$; as a result it is not dispersed in time as is desirable for a collision experiment.

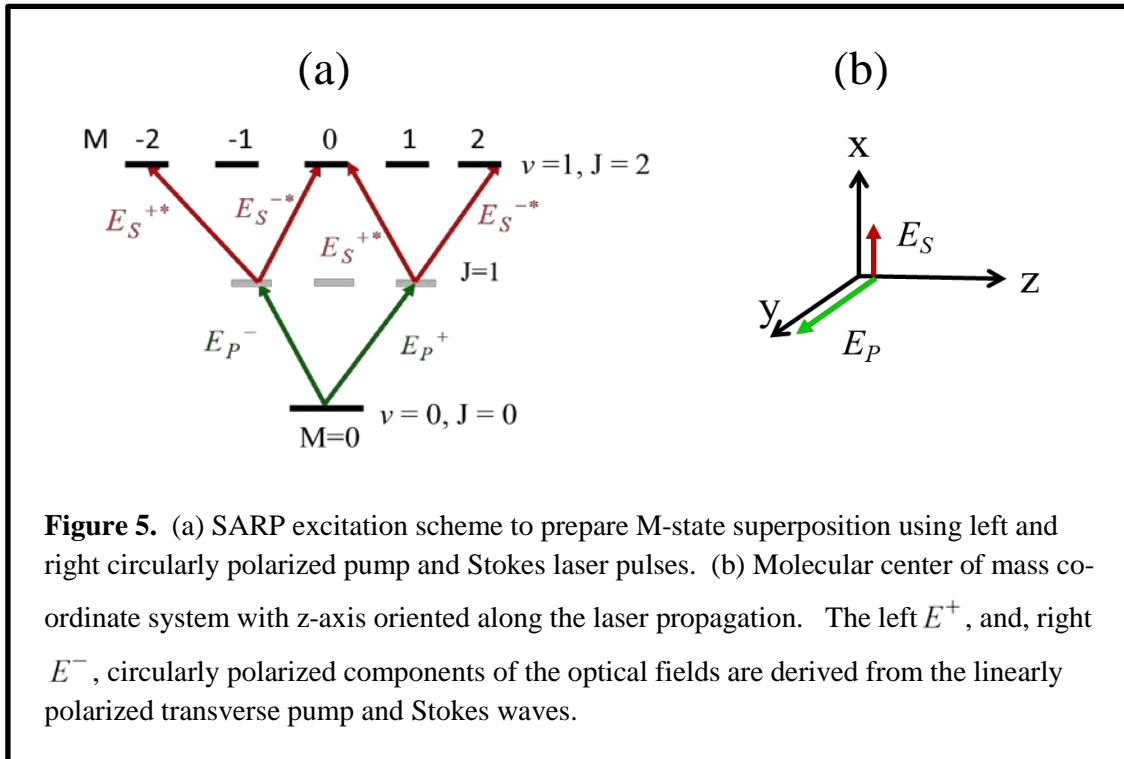
When the target is prepared in a superposition state given in Eq. (1), the state-resolved differential scattering cross-section will contain cross terms or interference terms as given below:

$$\frac{d\sigma(v', J', \theta, \varphi)}{d\Omega} = \left(\frac{d\sigma}{d\Omega} \right)_{\text{M-averaged}} + \sum_{M \neq M'} C_M^* C_{M'} Q_{MM'} \quad (2)$$

The second term in the right hand side of Eq. (2) $\propto C_M^* C_{M'}$ gives rise to interference in the collision probability. The maxima and minima of this interference are determined by the relative phase of the coefficients C_M . In other words, by controlling their relative phase, we can expect to control the outcome of a collision experiment. When a large ensemble of target molecules is prepared in a coherent superposition of eigenstates, the ensemble behaves like a multi-slit molecular interferometer in a scattering experiment. SARP thus opens completely new vistas of reaction dynamics which will allow us to study, for the first time, **the coherent** dynamical stereochemistry, where M-state **interference** controls the outcome of a scattering experiment.

Recently using SARP ($v=0, J=0$) \rightarrow ($v=1, J=2, M$) we experimentally prepared and detected such coherent superposition of M-states. The excitation scheme to create a biaxial superposition state with cross-polarized pump and Stokes laser pulses is shown Fig. 5. The biaxial state is given by:

$$|\psi(t)\rangle = 1/\sqrt{2} [|v=1, J=2, M=-2\rangle - |v=1, J=2, M=+2\rangle] \quad (3)$$



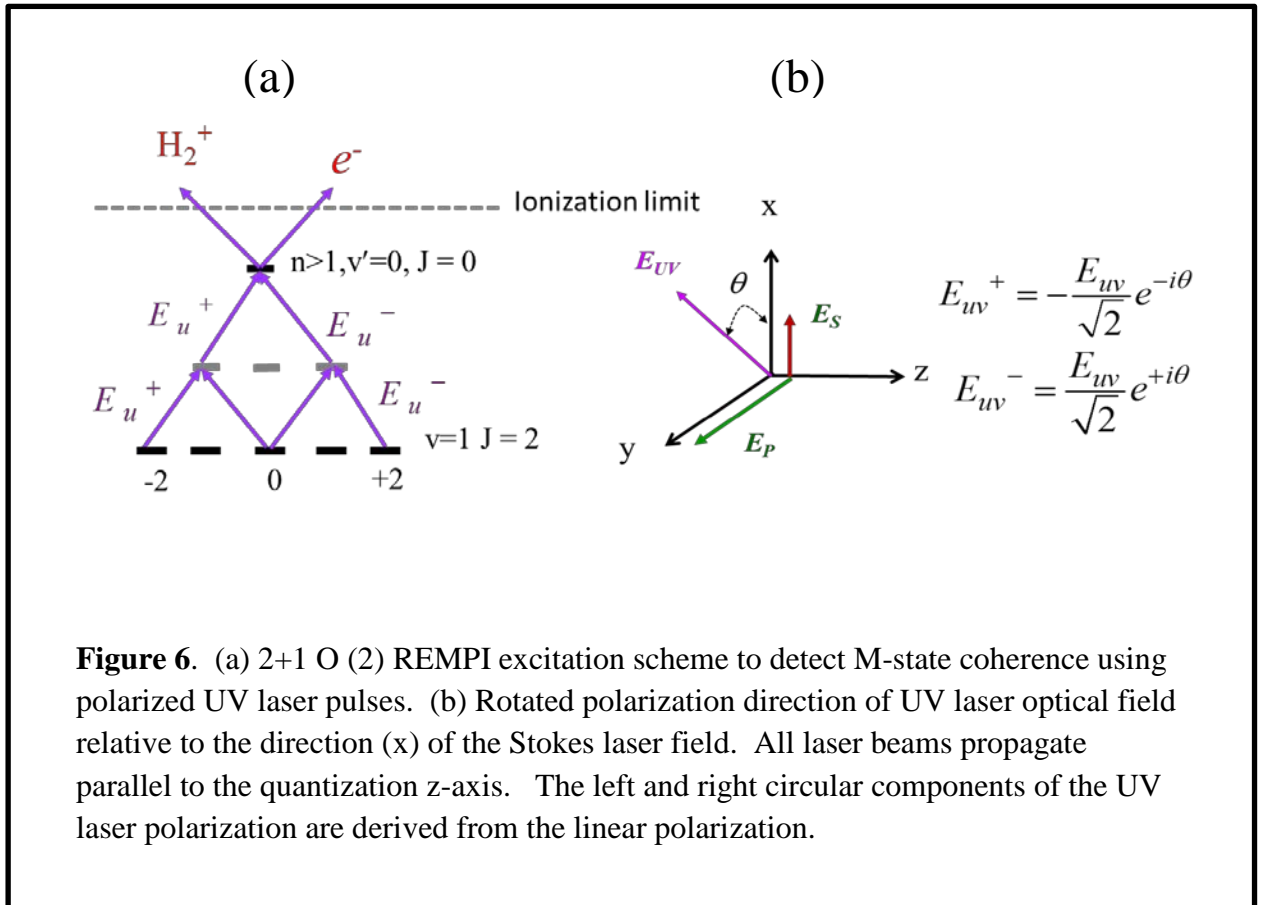
Similarly, with the parallel polarization of pump and Stokes laser pulses SARP creates the following uniaxial superposition state:

$$|\psi(t)\rangle = \sqrt{\frac{3}{8}} |v=1, J=2, M=-2\rangle - \frac{1}{2} |v=1, J=2, M=0\rangle + \sqrt{\frac{3}{8}} |v=1, J=2, M=+2\rangle \quad (4)$$

Using (2+1) REMPI probe we measured 60% population transfer from ($v=0, J=0$) to the M-state superposition within the rovibrational ($v=1, J=2$) energy state using parallel or perpendicular SARP.

Detection of M-state superposition using 2+1 O (2) REMPI:

To detect the M-state coherence ($C_M^* C_{M'}$) we exploit interference of the resonantly enhanced multiphoton ionization channels associated with $E, F^1\Sigma_g^+(v'=0, J'=0) \leftarrow X^1\Sigma_g^+(v=1, J=2)$ transition of O (2) branch as shown in Fig 6.



For the linearly polarized UV probe field at an angle θ with respect to the x-axis the 2+1 REMPI signal can be expressed as a function of θ :

$$O(2) \propto \left| C_- e^{+i2\theta} - \sqrt{\frac{2}{3}} C_0 + C_+ e^{-i2\theta} \right|^2 \quad (5)$$

In the following we present our recent experimental results detecting the coherent superposition of M-states by measuring the O(2) REMPI signal as the direction of UV polarization is rotated using a half-wave retarder. Figure 7(a) shows (2+1) O (2) REMPI signal as a function of the polarization angle θ of the UV probe laser pulse for the superposition state in Eq. (4) which is prepared by parallel SARP. Figure 7 (b) shows the angular momentum polarization.

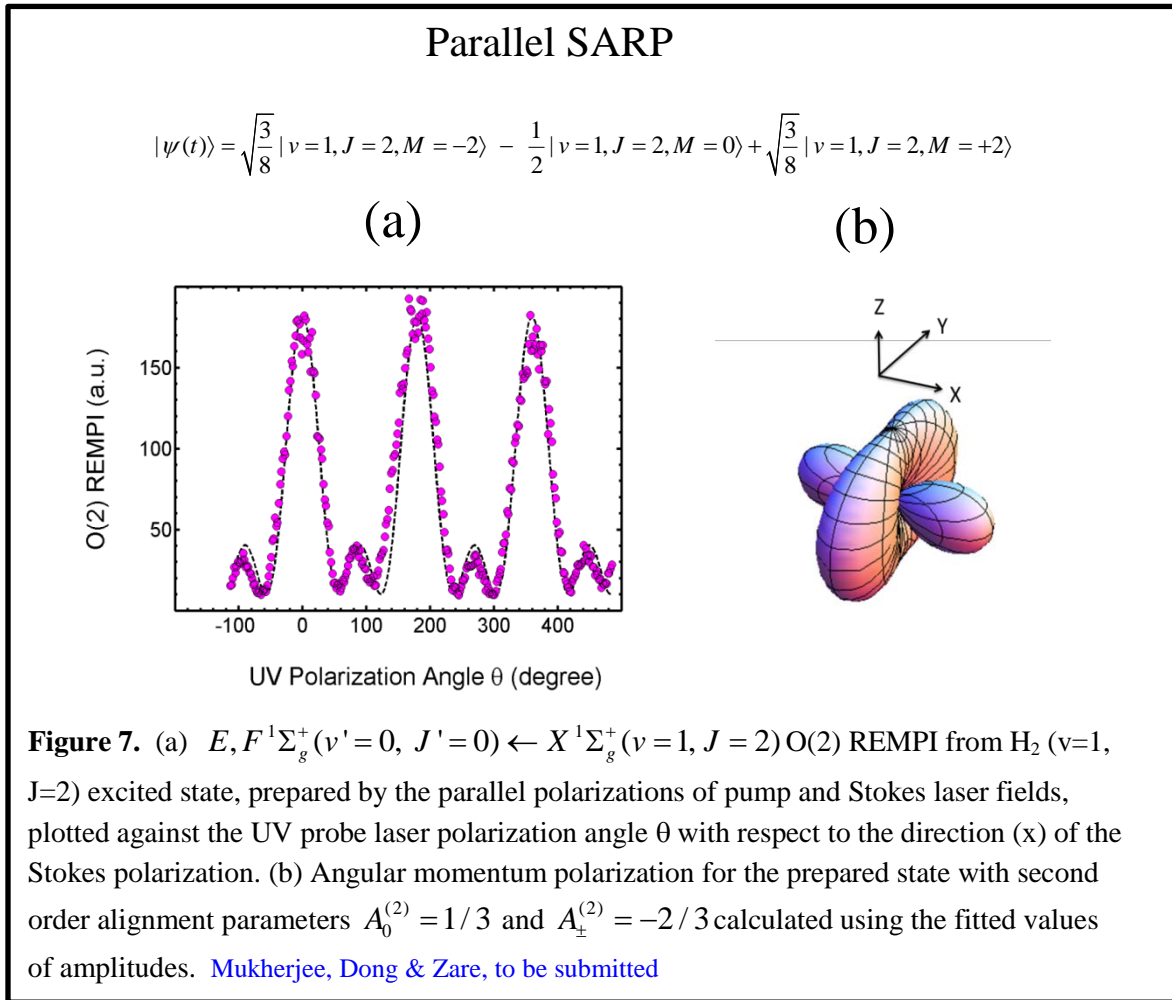
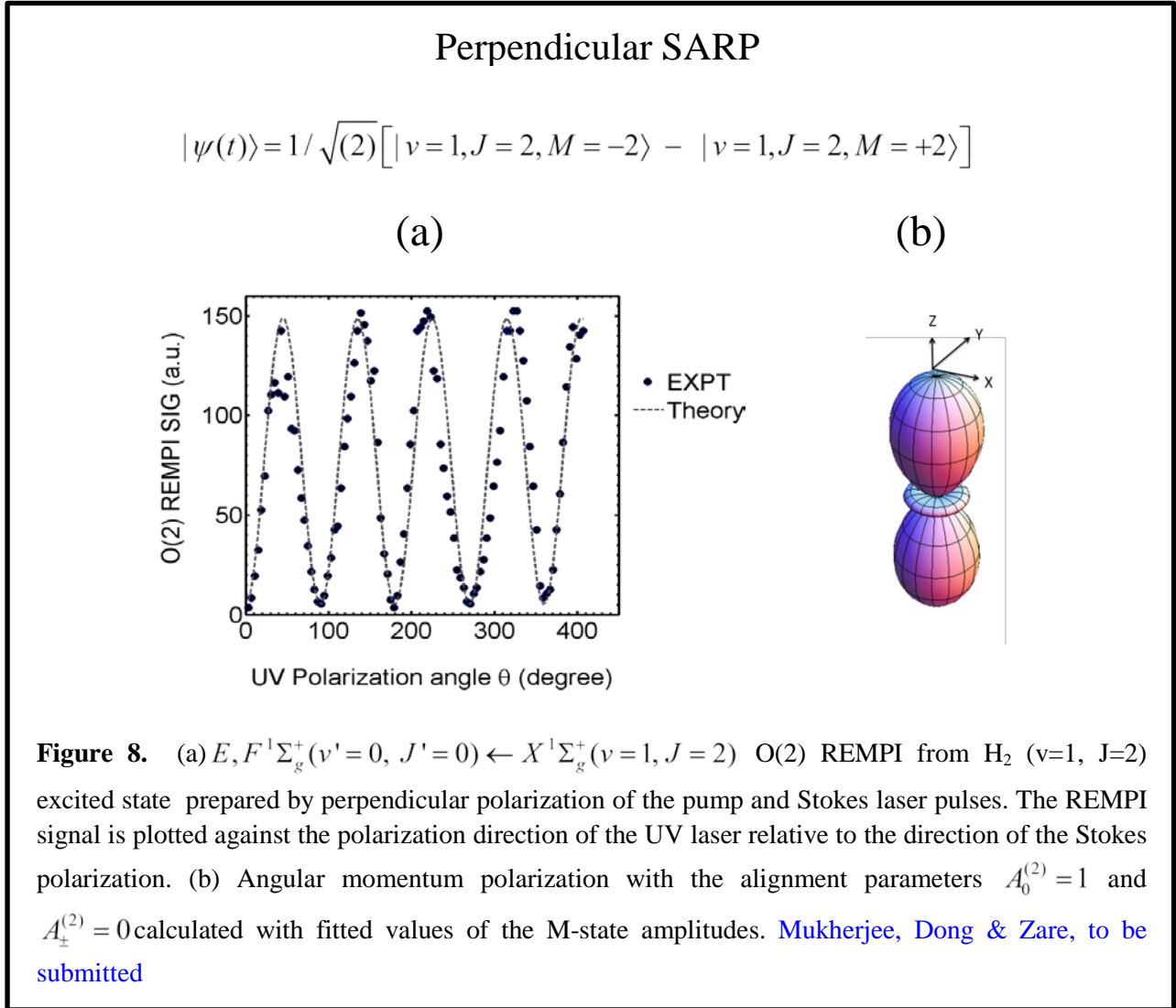


Figure 8(a) shows (2+1) O (2) REMPI signal as a function of the polarization angle θ of the UV probe laser pulse for the bi-axial superposition state in Eq. (3) which is prepared by combining cross polarized pump and Stokes laser pulses (excitation scheme of Fig. 5). Figure 8(b) shows the angular momentum polarization.



We believe SARP is a powerful tool to prepare molecules in desirable quantum states, and, it is particularly suitable for molecules having a wide energy gap (diatoms like H_2 , D_2 , HCl , N_2) between the ground and excited electronic states, where other adiabatic methods like STIRAP or SCRAP seemed difficult to apply. SARP should open for study a wealth of experiments involving coherently prepared reagents.